

UTILITY PATENT APPLICATION

OF

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FOR

ELECTROLYTE SYSTEM AND ENERGY STORAGE DEVICE USING SAME

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BACKGROUND OF THE INVENTION

Energy storage devices such as batteries that utilize the oxidation and reduction reactions of an alkali metal are known. Such "lithium ion cells" include secondary cells which use a carbon material that can be doped and undoped with lithium ions as a negative pole and which use a complex oxide of lithium and a second metal as a positive pole. Lithium ion cells are compact and lightweight, and have a high energy density. Accordingly, the use of lithium ion cells as secondary cells in portable electronic devices has expanded rapidly. Concurrently, there has been an escalating demand for improved performance, e. g., an increase in the energy density and an increase in the discharge current, etc., in lithium ion cells in order to achieve a further improvement in the function of such portable electronic devices.

The decreased size of such energy storage devices has resulted in the presence of highly energetic active substances in a small, confined volume. As a result, large amounts of energy can be released when electrodes short-circuit or otherwise fail as a result of, for example, piercing and compression that may cause a battery to ignite and catch fire. As the cell capacity has increased, there has been a strong demand for an improvement in battery safety.

Previous attempts to increase safety have been directed to changing electrode construction or changing the active substance. Other studies have focused on additives to the electrolyte solution that increase the safety of the batteries. Thus,

for example phosphorus and fluorine compounds such as triphenyl phosphate and fluoro-ethers have been dissolved in the electrolyte solution to improve battery safety. However, these compounds may be subject to oxidation-reduction by the electrodes, or may react with the electrodes so that the capacity is lowered. Although safety is improved when the amounts of additives are increased, battery performance deteriorates. Accordingly, it has been difficult to realize increased safety without causing a deterioration of conventional battery characteristics.

There is thus a continuing need for improved cell capacity, charge-discharge rate, and charge-discharge cycle.

There is also a continuing need for an improved battery with an improved safety profile that does not deteriorate over time.

SUMMARY OF THE INVENTION

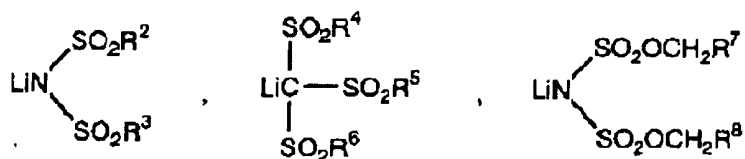
One object of the present invention is to provide an electrolyte system for an energy storage device that is extremely safe and has superior charge-discharge characteristics.

Another object of the present invention is to provide an electrolyte system of high conductivity and low viscosity for improving the discharge capacity of a secondary cell battery.

Another object of the present invention is to provide an electrolyte system that is chemically and electrically stable with respect to the positive pole and negative pole of the secondary cell battery.

In accordance with the present invention, an electrolyte system comprises a non-aqueous electrolyte solution including a non-aqueous solvent and a salt, and a flame retardant material that is a liquid at room temperature and pressure and that is substantially immiscible in the non-aqueous electrolyte solution.

The non-aqueous electrolyte solution is formed by dissolving a salt, preferably an alkali metal salt, in a non-aqueous solvent. The non-aqueous solvent is a polar aprotic organic solvent which readily dissolves alkali metal salts, and which is resistant to being electrolyzed by oxidation-reduction at the battery poles. The non-aqueous solvent preferably includes a cyclic carbonate and/or a linear carbonate, wherein the cyclic carbonate preferably contains an alkylene group with 2 to 5 carbon atoms, and the linear carbonate preferably contains a hydrocarbon group with 1 to 5 carbon atoms. Preferred electrolytes include LiPF_6 , LiBF_4 , LiOSO_2R^1 ,



(in the above formulae, R^1 through R^8 indicate perfluoroalkyl, alkyl or aryl groups with 1 to 6 carbon atoms, which may be the same or different groups). The

concentration of the electrolytes in the non-aqueous electrolyte solution is preferably between about 0.1 to 3.0 moles/liter, and more preferably between about 0.5 to 2.0 moles/liter.

5 The flame retardant material is a liquid at room temperature and pressure and is substantially immiscible in the non-aqueous electrolyte solution. Preferably, the flame retardant material is a halogen-containing compound. Preferred halogen-containing compounds contain perfluoroalkyl groups or perfluorether groups. The halogen-containing compound is present in an amount by weight of non-aqueous solvent in a range of from about 1 to about 99 wt %, preferably from about 1 to about 70 wt %, even more preferably from about 10 to about 60 wt % and even more preferably from about 20 to about 40 wt%.

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15 An energy storage device in accordance with the present invention comprises the disclosed electrolyte system, an electrode assembly including a first electrode member, a second electrode member, a separator member physically and electrically separating the first electrode member from the second electrode member but capable of allowing ionic conductivity between the first electrode member and the second electrode member through the non-aqueous electrolyte solution, and a casing enclosing the electrode assembly and the electrolyte system. In a energy storage device, such as a battery, the first electrode member is a negative electrode
20 containing a material selected from the group consisting of lithium metal, a lithium alloy, a carbon material that can be doped and undoped with lithium ions, a metal

~~oxide that can be doped and undoped with lithium ions, and silicon that can be~~

doped and undoped with lithium ions, the second electrode member is a positive electrode containing a material selected from the group consisting of complex oxide of lithium and a transition metal, and a complex oxide of lithium, transition metal
5 and a non-transition metal, and the separator member is a resin containing a polymer.

A method of making a energy storage device in accordance with the present invention comprises providing an electrode assembly including a first electrode member, a second electrode member and a separator member physically and electrically separating the first electrode member from the second electrode member but capable of allowing ionic conductivity between the first electrode member and the second electrode member, placing the assembly in a casing, and filling the casing with the electrolyte system of the present invention by first, filling the casing at least partially with the non-aqueous electrolyte solution, waiting a period of time
10 sufficient for the non-aqueous electrolyte solution to penetrate one or more pores of the electrode assembly, and then adding the flame retardant material to the casing.

In practice, the two phase electrolyte system of the present invention realizes significant advantages over the prior art. Because the halogen-containing compound is not miscible in the non-aqueous electrolyte solution, there is little
20 ingress of the halogen-containing compound into the regions within the casing occupied by the non-aqueous electrolyte solution, i.e. in the casing regions

separating the positive and negative poles and defined by the separator. As such,

there is little interference by the halogen-containing compound in electrochemical reactions occurring at the poles and in the non-aqueous electrolyte solution.

Further, the secondary cell is superior in terms of initial capacity and cycle

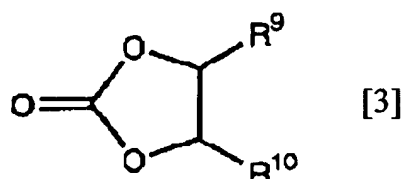
5 characteristics. Moreover, the halogen-containing compound of the present invention interferes and/or inhibits combustion reactions that may result upon piercing or compression of the battery. Accordingly, the energy storage device of the present invention exhibits enhanced safety over prior art secondary cells.

10 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

An electrolyte system for an energy storage device includes a non-aqueous electrolyte solution including a non-aqueous solvent and a salt, and a flame retardant material that is a liquid at room temperature and pressure and that is substantially immiscible in the non-aqueous electrolyte solution. The non-aqueous
15 electrolyte solution permits the exchange of metal ions between the positive pole and negative pole of the battery.

The non-aqueous electrolyte solution of the present invention is formed by dissolving a salt, preferably an alkali metal salt, in a non-aqueous solvent. The non-aqueous solvent of the present invention is preferably a polar aprotic organic
20 solvent which readily dissolves alkali metal salts, and which is resistant to being electrolyzed by oxidation-reduction at the poles.

~~The non-aqueous solvent of the present invention preferably includes one or~~
more cyclic carbonates of the following general formula:



5 where R⁹ and R¹⁰ may be the same or different, and may be hydrogen, a
linear alkyl group, a branched alkyl group, a cyclic alkyl group, or a halogen-
substituted alkyl group in which some or all of the hydrogen atoms are substituted
by at least one halogen selected from a set consisting of chlorine and bromine.
When linear alkyl groups are selected, linear alkyl groups with 1 to 4 carbon atoms
such as methyl groups, ethyl groups, propyl groups and butyl groups, etc., are
10 preferred. When branched alkyl groups are selected, branched alkyl groups with 3
to 10 carbon atoms, and especially 3 to 6 carbon atoms, such as isopropyl groups,
isobutyl groups, sec-butyl groups and tert-butyl groups, etc., are preferred. When
cyclic alkyl groups are selected, cyclic alkyl groups with 5 to 10 carbon atoms such
15 as cyclopentyl groups, cyclohexyl groups and 1-methylcyclohexyl groups, etc., are
preferred.

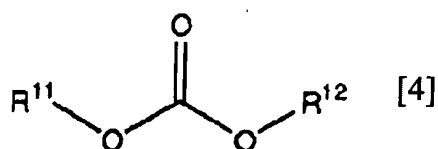
The non-aqueous solvent may include cyclic carbonates having 5-member
ring compounds as shown in above formula and 6-member ring compounds.
Examples of suitable cyclic carbonates include ethylene carbonate, propylene

carbonate, 1,2-butylene carbonate, 2,3-butylene carbonate, 1,3-propylene carbonate,

1,3-butylene carbonate, 2,4-pentylene carbonate, 1,3-pentylene carbonate and
vinylene carbonate, etc. Furthermore, halogen-substituted cyclic carbonates in
which some or all of the hydrogen atoms in the methyl groups of the aforementioned
5 propylene carbonates, etc., are substituted by at least one halogen selected from a
set consisting of fluorine, chlorine and bromine may also be used.

Preferably, the cyclic carbonate contains an alkylene group with 2 to 5 carbon
atoms. More preferably, ethylene carbonate and propylene carbonate are used.
Two or more such cyclic carbonates may be used in combination.

The non-aqueous solvent of the present invention may additionally include
one or more linear carbonates shown in the following general formula:



where R^{11} and R^{12} may be the same or different, and may be branched or cyclic alkyl
15 groups, or halogen-substituted alkyl groups in which some or all of the hydrogen
atoms are substituted by at least one halogen selected from a set consisting of
fluorine, chlorine and bromine. When a linear alkyl group is selected, linear alkyl
groups with 1 to 4 carbon atoms such as methyl groups, ethyl groups, propyl groups
and butyl groups, etc., are preferred. When branched alkyl groups are selected,

branched alkyl groups with 3 to 10 carbon atoms, such as isopropyl groups, isobutyl groups, sec-butyl groups and tert-butyl groups, etc., are preferred. When cyclic alkyl groups are selected, cyclic alkyl groups with 5 to 10 carbon atoms such as cyclopentyl groups, cyclohexyl groups and 1-methylcyclohexyl groups, etc., are preferred.

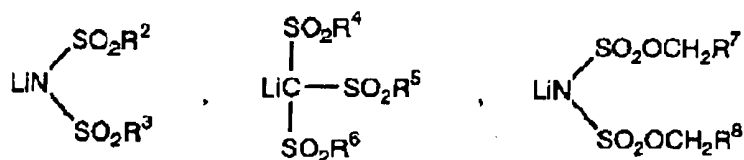
Examples of suitable linear carbonates include dimethyl carbonate, diethyl carbonate, di-n-propyl carbonate, dibutyl carbonate, diisopropyl carbonate and methylethyl carbonate, etc. Among such linear carbonates, linear carbonates that contain a hydrocarbon group with 1 to 5 carbon atoms are desirable in the present invention, and dimethyl carbonate, methylethyl carbonate and diethyl carbonate are especially desirable.

The non-aqueous solvent of the present invention may also include one or more solvents selected from the group consisting of cyclic esters such as γ -butyrolactone, γ -valerolactone, 3-methyl- γ -butyrolactone and 2-methyl- γ -butyrolactone, etc., linear esters such as methyl formate, ethyl formate, methyl acetate, ethyl acetate, propyl acetate, methyl propionate, methyl butyrate and methyl valerate, etc., cyclic ethers such as 1,4-dioxane, 1,3-dioxolane, tetrahydrofuran, 2-methyltetrahydrofuran, 3-methyl-1,3-dioxolane and 2-methyl-1,3-dioxolane, etc., linear ethers such as 1,2-dimethoxyethane, 1,2-diethoxyethane, diethyl ether, dimethyl ether, methylethyl ether and dipropyl ether, etc., sulfur-containing compounds such as sulfolane and dimethyl sulfate, etc., and phosphorus-

containing compounds such as trimethylphosphoric acid and triethylphosphoric acid, etc.

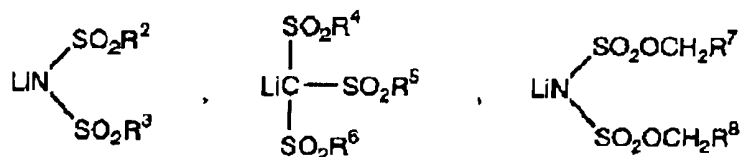
The non-aqueous solvent of the present invention may be one solvent used singly or may be a mixture consisting of two or more solvents.

5 One or more salts are dissolved in the non-aqueous solvent in order to prepare the non-aqueous electrolyte solution of the present invention. Preferably, the concentration of the salts in the non-aqueous electrolyte solution is between about 0.1 to 3.0 moles/liter, and more preferably between about 0.5 to 2.0 moles/liter. The salt used in the present invention may be any salt known to those of ordinary skill in the art to be used in non-aqueous electrolyte solutions of energy storage devices such as secondary cells. The salt may be a single salt or a mixture of salts. Suitable examples of salts include lithium salts such as LiPF_6 , LiBF_4 , LiClO_4 , LiAsF_6 , LiAlCl_6 , Li_2SiF_6 , LiOSO_2R^1 ,
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where R¹ through R⁸ may be the same or different, and are perfluoroalkyl, alkyl or aryl groups with 1 to 6 carbon atoms, and alkali metal salts in which the lithium in the above-mentioned salts is substituted by alkali metals. These compounds may be used singly or in mixtures consisting of two or more compounds.

Preferred electrolytes are LiPF₆, LiBF₄, LiOSO₂R¹;



The electrolyte system of the present invention further includes a flame retardant material. A suitable flame retardant material is liquid at room temperature and pressure, is substantially anhydrous and is substantially immiscible with the electrolyte solution. Substantially immiscible means that when the non-aqueous electrolyte solution and the halogen-containing compound are mixed, a meniscus between the two liquids is formed and the concentration of the

halogen-containing compound in the non-aqueous electrolyte solution is about 10 wt

% or less and preferably, 1000 ppm or less. More preferably, the flame retardant material is completely immiscible in the non-aqueous electrolyte solution. Suitable flame retardant materials are stable with respect to electro-chemical reactions on the electrodes, and are chemically inert with respect to the electrolyte and the non-aqueous solvent in the battery environment. Suitable flame retardant materials are further characterized by having very low vapor pressure at room temperature.

Preferably, the flame retardant material is a halogen containing compound. Suitable halogen-containing compounds include branched or unbranched alkyls, cyclic alkyls, ethers, amino alkyls, aliphatic heterocyclic compounds in which one or more of the hydrogen atoms are substituted with a halogen atom selected from the group consisting of fluorine, chlorine and bromine. In general, increasing efficacy is obtained with increases in the number of halogen atoms. Preferably, the halogen-containing compounds include perfluoroamine and perfluoroether compounds. Preferred halogen-containing compounds include perfluoro-1,3-dimethylcyclohexane and FC-70, sold under the trade name Fluorinert, having a molecular formula $C_{15}F_{33}N$, and commercially available from 3M Co. of St. Paul, Minnesota.

Preferably, the halogen-containing compound is present in an amount by weight of non-aqueous solvent in a range of from about 1 to about 99% by weight of non-aqueous solvent, preferably in a range of from about 1 to about 70% by weight of non-aqueous solvent, more preferably from about 10 to about 60% by weight of

non-aqueous solvent, and even more preferably from about 20 to about 40% by weight of non-aqueous solvent.

In the electrolyte systems of the present invention, the use of the halogen-containing compound and a cyclic carbonate and/or linear carbonate is especially preferred. In cases where a halogen-containing compound and a cyclic carbonate and/or linear carbonate is used, the halogen-containing compound is preferably present in an amount by weight of non-aqueous solvent ranging from about 1 to about 99 wt %, preferably from about 1 to about 70 wt %, more preferably from about 10 to about 60 wt %, and even more preferably from about 20 to about 40 wt %. Furthermore, it is desirable that the aforementioned cyclic carbonate and/or linear carbonate be contained in the non-aqueous solvent in an amount from about 1 to 99 wt %, preferably from about 30 to 99 wt %, and even more preferably from about 40 to 90 wt %.

The electrolyte system of the present invention is used in connection with an electrode assembly and a casing to produce an energy storage device such as a battery. An energy storage device according to the present invention comprises an electrolyte system in accordance with the present invention, an electrode assembly, the electrode assembly including a first electrode member, a second electrode member; and a separator member physically and electrically separating the first electrode member from the second electrode member but capable of allowing ionic conductivity between the first electrode member and the second electrode member

through the non-aqueous electrolyte solution, and a casing enclosing the electrode assembly and the electrolyte system.

10 112 Preferably the energy storage device in accordance with one embodiment of the present invention is a battery in which the first electrode member is a negative electrode containing a material selected from the group consisting of lithium metal, 5 a lithium alloy, a carbon material that can be doped and undoped with lithium ions, a metal oxide that can be doped and undoped with lithium ions, and silicon that can be doped and undoped with lithium ions. Preferably the metal oxide is tin oxide and titanium oxide. Preferably, a carbon material that can be doped and undoped with 10 lithium ions is used as the negative pole. Suitable carbon for the negative pole includes graphite or amorphous carbon, activated carbon, carbon fibers, carbon black and meso-carbon, micro-beads, etc.

15 In this embodiment, the second electrode member is a positive electrode containing a material selected from the group consisting of complex oxide of lithium and a transition metal, and a complex oxide of lithium, transition metal and a non-transition metal. Suitable materials include complex oxides of lithium and transition metals, such as LiCoO_2 , LiMnO_2 , LiMn_2O_4 , LiNiO_2 and $\text{LiNi}_x\text{Co}_{(1-x)}\text{O}_2$, etc., and V_2O_5 , etc.

The separator member may be a porous polymer or ceramic material.

20 Preferably, the separator is a resin containing a polymer, generally a microporous polymer film. Suitable examples include polyesters, polyacetyl and polyethylene.

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Energy storage devices may be prepared using the electrolyte system of the present invention as follows. A method of making an energy storage device in accordance with the present invention comprises providing an electrode assembly including a first electrode member, a second electrode member, and a separator member physically and electrically separating the first electrode member from the second electrode member but capable of allowing ionic conductivity contact between the first electrode member and the second electrode member, placing the assembly in a casing, and filling the casing with the electrolyte system that is herein described, filling the casing at least partially with the non-aqueous electrolyte solution, waiting a period of time sufficient for the non-aqueous electrolyte solution to penetrate one or more pores of the electrode assembly, and then adding the flame retardant material to the casing.

The energy storage devices of the present invention may take any suitable shape or configuration, including a battery of suitable shape and configuration, including a coin type battery, a prismatic battery, a stacked battery, cylindrical battery, etc.

Within the battery casing, the non-aqueous electrolyte solution selected in accordance with the present invention and the halogen-containing compound selected in accordance with the present invention form two separate liquid phases. Since the non-aqueous electrolyte solution and the halogen-containing compound are substantially immiscible, one liquid phase within the battery casing is mainly

non-aqueous electrolyte solution and the other liquid phase in the battery casing is
mainly halogen-containing compound. In accordance with the present invention,
the non-aqueous electrolyte solution phase occupies the region within the casing
between the positive pole and the negative pole defined by the separator. As a
5 result, the halogen-containing compound is not in the region between the positive
pole and the negative pole defined by the separator and does not interfere with the
oxidation-reduction processes at the poles and in the non-aqueous electrolyte
solution. However, the halogen-containing compound tends to inhibit the
occurrence of highly energetic events such as combustion processes and therefore
10 increases battery safety. Applicant believes the halogen-containing compound may
interfere with the production of highly energetic and highly reactive carbon radicals
produced in combustion processes and/or interfere with chain reaction processes by
production of fluoride radicals.

The following examples are illustrative of certain embodiments of the
15 invention and are not to be construed as limiting the invention thereto.

Example 1

A positive pole prepared from LiCoO_2 and PVDF (poly(vinylidene
fluoride)) and a negative pole prepared from graphite and PVDF (poly(vinylidene
20 fluoride)) were fastened together with a separator (manufactured by Tonen)

between them, thus producing an electrode assembly. The assembly was then introduced into a battery casing.

A non-aqueous electrolyte solution was prepared by mixing ethylene carbonate (EC), diethyl carbonate (DEC) and LiPF_6 in a weight ratio of EC to DEC to LiPF_6 of 21.84 wt%: 37.59 wt%: 10.57 wt%. The non-aqueous electrolyte solution was then introduced into the battery casing. After waiting 1 hour, the flame retardant material, a halogen-containing compound, perfluoro-1,3-dimethylcyclohexane was then introduced into the battery casing at a 30% weight ratio of halogen-containing compound to electrolyte solution.

The battery was sealed and charged at 0.1 C to a charge of 4.3 V by constant-current constant-voltage charging. The battery was then discharged at a constant current and the discharge capacity and safety level measured. The results are shown in Table 1.

Example 2

A non-aqueous electrolyte solution and battery were prepared in the same manner as in Example 1, except that FC-70 was used as the halogen-containing compound. The battery discharge capacity and safety level were measured and the results are shown in Table 1.

Comparative Example 1

~~A non-aqueous electrolyte solution was prepared in the same manner as in~~

Example 1, except that a halogen-containing compound was not added to the electrolyte solution. The battery discharge capacity and safety level were measured and the results are shown in Table 1.

5 The safety of the energy storage devices was assessed using an "Overcharge Test." The above examples were overcharged at a 4.4-4.5 V. The temperature on the outside of the battery casing was measured. Overcharging was continued until the battery became mechanically detached or until the temperature of the battery casing peaked and began to decrease. Safety was assessed according to a 4 level
10 designation:

Level 1: Maximum Casing Temperature less than 80°C

Level 2: Maximum Casing Temperature between 80°C and 120°C

Level 3: Maximum Casing Temperature over 120°C

Level 4: Mechanical Detachment

15 As indicated by the results tabulated in Table 1, addition of the halogen-containing compound to the non-aqueous electrolyte solution significantly improved the safety level of the battery (from "4" to either "2" or "1") without adversely affecting the discharge capacity of the battery to any significant degree.

20 The principle preferred embodiments and modes of operation of the present invention have been described. The invention described herein, however, is not intended to be construed as limited to the particular forms disclosed, since they are

Table 1

Additive name	Discharge capacity(%)	Safety level	EC ratio(wt%)	DEC ratio(wt%)	LiPF6 ration(wt%)	Additive ratio(%)
none	100.0	4	31.2	53.7	15.1	0
perfluoro-1,3-dimethylcyclohexane	96.3	1	21.84	37.59	10.57	30
	93.7	2	21.84	37.59	10.57	30
FC-70	99.5	2	21.84	37.59	10.57	30
	100.5	2	21.84	37.59	10.57	30